



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/US94/08368 (22) International Filing Date: 25 July 1994 (25.07.94) (30) Priority Data: 08/098,493 27 July 1993 (27.07.93) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: NEMSER, Stuart, Marshall; 325 Hampton Road, Wilmington, DE 19803-2425 (US). (74) Agents: LEVITT, Cary, A. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p>		<p>(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: MEMBRANE CLOSURE DEVICE</p> <p>(57) Abstract</p> <p>The invention is a membrane closure apparatus comprising a selectively permeable gas separation membrane (8) having a feed side which is in communication with an organic gas in a fuel or storage tank (6). The apparatus is particularly useful as a means for closing the filler tube (2) or vent line of a fuel tank or storage tank. The gas separation membranes which may be used with the apparatus are not limiting; however, a preferred membrane may be formed from amorphous polymers of perfluoro-2,2-dimethyl-1,3-dioxole, especially copolymers with a complementary amount of at least one of tetrafluoroethylene, perfluoromethyl vinyl ether, vinylidene fluoride and chlorotri-fluoroethylene. More preferably, the polymer is a dipolymer containing 65-99 mole % of perfluoro-2,2-dimethyl-1,3-dioxole and having a glass transition temperature of at least 140 °C.</p>		



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**TITLE****MEMBRANE CLOSURE DEVICE****FIELD OF THE INVENTION**

5 The present invention relates to closure devices such as a check valve or relief valve which incorporate selectively permeable membranes formed from a polymer. Such valves may be advantageously used with underground storage tanks, above-ground storage tanks, automotive fuel tanks, automotive filler necks, ventilating devices and the like.

**BACKGROUND OF THE INVENTION**

10 This invention relates generally to means for closing the filler tube or vent line of containers such as fuel tanks, underground storage tanks and above-ground storage tanks and the like, and more particularly to a safety-type closure assembly which prevents fuel vapors from escaping from the tank at the time of refueling a vehicle or pumping fuel into a tank or  
15 container.

Check valves and relief valves are well known. They may also be referred to as pressure relief valves, expiration valves or controllable expiration valves. Such valves are useful to trap or seal-in vapors or gaseous emissions from a tank or vessel storing a gas or liquid. However, such valves  
20 disadvantageously permit the release of noxious fumes.

For example, in conventional-type fuel systems for motor vehicles, a vented type of filler cap is screwed on or otherwise secured to the outer end of a filler tube to prevent fuel loss from the fuel tank. The filler caps take many forms and some even include filter elements which operate  
25 to filter incoming air and/or prevent dirt from entering relief valve assemblies while in position on the filler tube.

However, when one proceeds to refuel or otherwise add fuel to the tank, the filler cap must be removed and the operator must then insert a fuel delivery nozzle into the top of the filler tube which at the same time  
30 opens a spring-loaded flap valve located at the outer end of the filler tube. In doing so and during the course of a filling procedure, fuel vapors in the tank and the filling tube rise and escape to the surrounding environment. The resulting fumes not only cause air pollution, but create an explosion or fire hazard, have a noxious effect on the person(s) in the immediate vicinity,  
35 can result in sickness and headaches in persons breathing the vapors and in some cases eventually causes and/or aggravates respiratory illnesses in such person(s).



U.S. Patent No. 5,042,678 provides an improved closure for fuel tanks. The closure was designed to prevent the outflow of organic vapors from a tank during filling. The closure comprises a housing which is essentially cylindrical with a central axial opening. The axial opening  
5 permits the passage of the fuel delivery nozzle therethrough. The cylindrical housing contains an elastically resilient fuel vapor absorbent filter element having a central circular opening which is selected to be slightly less than the delivery of the fuel delivery nozzle. However, the filter element may become saturated which impairs its effectiveness and, therefore, must be  
10 periodically replaced. Moreover, conventional filter elements may not readily permit the expiration of air during the filling operation, thereby prolonging the filling operation and increasing the risk of explosion. For the same reason, the use of such filter elements may not be satisfactory in conjunction with check valves, pressure relief valves, expiration valves or the  
15 like.

A closure assembly for fuel tanks and the like is therefore needed which is of simple construction, permits outflow of air but prevents outflow of organic vapors, functions for long periods of time so that it does not require periodic replacements and retains the advantages of prior art  
20 devices.

#### SUMMARY OF THE INVENTION

The present invention is a closure assembly which may be engageable with the filler tube of a tank such as a fuel tank or the vent line of a storage tank for preventing the outflow of organic vapors from the tank  
25 during a filling procedure or venting of the tank. The closure assembly comprises a gas separation membrane which selectively permits the permeation of nitrogen and/or oxygen but not organic vapors. The gas separation membranes are preferably a bundle of hollow-fiber membranes. The bundle may have a central axial opening therein for permitting the  
30 passage of a fuel delivery nozzle therethrough.

The gas separation membranes may be formed from polymers which preferentially permit the permeation of nitrogen and/or oxygen in favor of organic vapors. The preferred membrane of the present invention is formed from an amorphous polymer of perfluoro-2,2-dimethyl-1,3-dioxole.  
35 The membrane is preferably a supported membrane, in the form of a film or coating on a porous support, or preferably in the form of a hollow fiber. In a



preferred embodiment the selective permeation of nitrogen over organic compounds, such as hydrocarbons, is at least 10:1.

Furthermore, the present invention provides a method for selectively closing or sealing a tank storing a gas or liquid, especially

5 hydrocarbons in a fuel tank, said method comprising:

- (a) providing in a membrane closure assembly a selectively permeable membrane, said membrane preferably having a nitrogen/hydrocarbon selectivity of at least 10;
- (b) a pressure differential develops across the membrane; and
- 10 (c) from the permeate side of the membrane, a gaseous admixture that is depleted in hydrocarbon vapors expires or is removed.

In preferred embodiments of the membranes and methods of the present invention, the polymer is a copolymer of perfluoro-2,2-dimethyl-1,3-dioxole, especially a copolymer having a  
15 complementary amount of at least one monomer selected from the group consisting of tetrafluoroethylene, perfluoromethyl vinyl ether, vinylidene fluoride and chlorotrifluoroethylene. In other embodiments, the polymer is a homopolymer of perfluoro-2,2-dimethyl-1,3-dioxole.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

20 Figure 1 is a schematic representation of a process for the separation of gaseous mixtures using a selectively permeable membrane.

Figure 2 is a schematic representation of a fuel tank filler tube closure assembly.

Figure 3 is a schematic representation of the membrane  
25 separation cell used in the filler tube closure assembly shown in Figure 2.

Figure 4 is a schematic representation of a membrane expiration valve for a fuel storage tank.

Figure 5 is a schematic representation of the membrane separation cell used in the expiration valve shown in Figure 4.

#### **DESCRIPTION OF THE INVENTION**

30 The closure assembly may use a polymer membrane which is in the form of a film or coating on a porous support or preferably a hollow fiber. An apparatus for a hollow-fiber membrane separation process is schematically illustrated in Figure 1. In that apparatus, membrane  
35 separation cell A has a feed or upstream section B and a permeate section C that are separated by selectively permeable membrane D. Feed section B has connected thereto an inlet pipe E. In addition, inlet section B has



connected thereto an outlet pipe F. Permeate section C is connected to outlet transfer line G.

In operation, a gaseous admixture containing organic vapors is fed through inlet pipe E to feed section B of membrane separation cell A.

- 5 The gaseous admixture may be at any temperature, preferably a temperature below the glass transition temperature of the polymer used to form the membrane. After a period of time, a hold-up time which will depend primarily on the flow rate of the gaseous admixture and the volume of the feed section, the portion of the gaseous admixture, primarily organic vapors,  
10 that has not passed through the selectively permeable membrane D will pass from the feed section B by means of outlet pipe F.

- The gaseous material passing through the selectively permeable membrane, which is depleted in organic vapors, passes from permeate section C through outlet transfer line G. Outlet transfer line G might be  
15 vented directly or indirectly to the atmosphere; as described herein, the gaseous admixture in outlet transfer line G will have substantially less of the gaseous organic compound than the inlet feed stream, and it might be environmentally acceptable to vent outlet transfer line G to the atmosphere.

- As will be appreciated by persons skilled in the art, the feed  
20 section of the membrane cell may be pressurized; eg., be at a pressure above atmospheric pressure as a result of periodic filling of the tank or pressure increases resulting from heating or reacting of the contents of the tank. In addition, a sweep gas or other means may be used on the feed side of the membrane so as to prevent the formation of a concentration gradient; i.e.,  
25 increased concentration of the organic vapors on the feed side of the membrane, which may impair the permeation properties of the membrane. The system may also be designed, as is known by those skilled in the art, to prevent liquid formation on the surface of the membrane which may disadvantageously retard flow of gases through the membrane.

- 30 Figure 2 depicts a membrane closure assembly for the filler neck of a fuel tank in accordance with a preferred embodiment of the invention. The filler tube 2 for the fuel tank 6 is customarily covered by a conventional gas cap, for example a threaded cap (not shown). The filler tube 2 having an opening 4 is shown including a well known spring-loaded flap valve 12. The  
35 spring-loaded flap valve 12 may be located in front of or behind the membrane separation cell 8. The spring-loaded valve may have one or more vent openings for equalizing pressure in the fuel tank 6.



The membrane separation cell 8, shown in greater detail in Figure 3, has a central opening 9, preferably a circular opening, and a plurality of hollow fiber membranes 7. The circular opening 9 is of a predetermined size to receive a fuel delivery nozzle. The circular opening 9 is defined by cylindrical structure 13 which is made from a material which is impermeable to the gaseous admixture in the tank 6. The circular opening 9 of the membrane separation cell may also comprise an elastically resilient material or the like which forms a secure seal around the fuel delivery nozzle when it is inserted into the filler tube 2. The membrane separation cell may be held in place within the filler tube 2 by any suitable means, for example by a retaining ring.

The membrane separation cell 8 is characterized by having at least one end of each of the hollow fiber membranes 7 embedded in a solid material in a fluid-tight manner to form tubesheets 14 and 15. These tubesheets 14 and 15 are typically composed of a potting material, typically a crosslinkable epoxy resin, which provides support for the hollow fibers 7, mechanical integrity to withstand operating pressure and temperature conditions, chemical resistance, and imparts a tight seal to prevent fluid communication between the exterior side and the bore side of each of the hollow-fiber membranes except through the walls of the hollow-fiber membranes. The potting material and the embedded hollow-fiber membranes are referred to as a tubesheet.

During fabrication, the hollow fibers may be placed in communication with the outside by slicing the tubesheet so as to cut off the loops of fiber projecting therefrom.

A tubesheet is usually formed near at least one end of the hollow-fiber membrane bundle. In operation, the tubesheets are preferably sealingly engaged with the inside of the filler tube 2 by, for example, O-rings 18. The tubesheet, the filler tube 2 and the hollow-fiber membranes together define a space external, typically an annular space, to membranes.

During operation, the gaseous admixture containing organic vapors flows into the open bores of the hollow-fiber membranes in tubesheet 14. The nonorganic components of the gaseous admixture will readily permeate through the selectively permeable membrane. Such gas will accumulate in annular space 17, which is in fluid communication with permeate discharge port 11. Preferably, permeate discharge port 11 is



vented to the atmosphere. Very little organic vapors are discharged to the atmosphere.

5 The organic components of the gaseous admixture do not readily permeate through the membranes. The gas enriched in organic components is collected in a manifold area 16 which is in fluid communication with the bores of the hollow fibers 7. Such gas is discharged via discharge port 10, which is preferably in fluid communication with the tank 6, so as to permit recycle of the organic enriched gas. The organic vapors may also be disposed of or filtered by other means well known in the art.

10 Figure 4 depicts a membrane closure assembly for the vent line 22 of a storage tank 26. The vent pipe 22 for the storage tank 26 comprises a membrane separation cell 28.

15 The membrane separation cell 28, shown in greater detail in Figure 5, has a plurality of hollow fiber membranes 27. The membrane separation cell may be held in place within the vent pipe by any suitable means, for example by a retaining ring. The membrane separation cell 28 is characterized by having at least one end of each of the hollow fiber membranes 27 embedded in a solid material in a fluid-tight manner to form tubesheets 34 and 35.

20 In operation, the tubesheets 34 and 35, are sealingly engaged with the inside of the vent pipe 22. The tubesheets, 34 and 35, the vent pipe 22 and the hollow-fiber membranes 27 together define a space external, typically an annular space 38, to membranes.

25 During operation, the gaseous admixture from the storage tank containing organic vapors flows into the open bores of the hollow-fiber membranes in tubesheet 34. The nonorganic components of the gaseous admixture will readily permeate through the selectively permeable membrane. Such gas will accumulate in annular space 38, which is in fluid communication with permeate discharge port 31. Preferably, permeate discharge port 31 is vented to the atmosphere. Very little organic vapors are discharged to the atmosphere.

30 The organic components of the gaseous admixture do not readily permeate through the membranes. The gas enriched in organic components is collected in a manifold area 36 which is in fluid communication with the bores of the hollow fibers 27. Such gas is discharged via discharge port 30, which is preferably in fluid communication with the tank 26 (not shown in



Figure 5), so as to permit recycle of the organic enriched gas back to the storage tank.

5 The membrane separation cell may also be placed within an independent shell or housing which may be then readily placed or inserted within the filler tube or vent line. The shell or housing may be fabricated from metal, ceramics, plastic, elastomers, or other materials known in the art.

The membrane separation cell may also be used in conjunction with conventional valves such as a check valve or pressure relief valve.

10 The membrane separation cell is not limited to any particular configuration of a hollow-fiber membrane separation device. However, a cylindrical configuration is preferred. The shell side of the permeator generally operates at atmospheric pressure. One knowledgeable in the membrane field would recognize that other configurations for the  
15 membrane separation cell are feasible. For example, hollow fibers may be arranged such that both ends of the fiber protrude through a single tubesheet or a single central tubesheet may also be used. Also, the bundle of membranes may have a noncircular cross-section with nonuniform packing density of membranes.

20 It should be noted that a number of separation devices can be stacked or connected in parallel or series to increase capacity and/or to improve separation. The skilled artisan can readily adapt the teachings herein to such configurations.

25 In addition, the potting material used to form the tubesheet may be comprised of any suitable material. Advantageously, this invention enables a wide range of materials to be employed as the potting material. Preferably the potting material can be in an essentially liquid form when preparing the tubesheet and can thereafter be solidified; e.g., by cooling, curing, or the like. The solidified potting material should be relatively inert  
30 to moieties to which it will be exposed during fluid separation operation.

The selectively permeable membrane may be formed from a wide variety of polymeric materials. The membranes for gas separation, according to the invention, can be films or hollow filaments, or fibers, having a porous separation membrane, or substrate, and a coating in contact with  
35 the porous separation membrane. Some factors which influence the behavior of the membranes are the permeability constants of the materials of the coating and porous separation membranes, the total cross-sectional



area of the holes (i.e., pores or flow channels) relative to the total surface area of the porous separation membrane, the relative thickness of each of the coating and the porous separation membrane of the membrane, the morphology of the porous separation membrane, and most importantly the relative resistance to permeate flow of each of the coating and the porous separation membrane in a multicomponent membrane. In general, the degree of separation of the gas separation membrane is influenced by the relative resistance to gas flow for each gas in the gas mixture of the coating and the porous separation membrane, which can be specifically chosen for their gas flow resistance properties.

The material used for the porous separation membrane may be a solid natural or synthetic substance having useful gas separation properties. In the case of polymers, both addition and condensation polymers which can be cast, extruded or otherwise fabricated to provide porous separation membranes are included. The porous separation membranes can be prepared in porous form, for example, by casting from a solution comprised of a good solvent for the polymeric material into a poor or nonsolvent for the material. The spinning and/or casting conditions and/or treatments subsequent to the initial formation, and the like, can influence the porosity and resistance to gas flow of the porous separation membrane.

Generally organic or organic polymers mixed with inorganics are used to prepare the porous separation membrane. Typical polymers suitable for the porous separation membrane according to the invention can be substituted or unsubstituted polymers and may be selected from polysulfones; poly(styrenes), including styrene-containing copolymers such as acrylonitrilestyrene copolymers, styrene-butadiene copolymers and styrene-vinylbenzylhalide copolymers; polycarbonates; cellulosic polymers, such as cellulose acetate-butyrate, cellulose propionate, ethyl cellulose, methyl cellulose, nitrocellulose, etc.; polyamides and polyimides, including aryl polyamides and aryl polyimides; polyethers; poly(arylene oxides) such as poly(phenylene oxide) and poly(xylene oxide); poly(esteramide-diisocyanate); polyurethanes; polyesters (including polyarylates), such as poly(ethylene terephthalate), poly(alkyl methacrylates), poly(acrylates), poly(phenylene terephthalate), etc.; polysulfides; polymers from monomers having alpha-olefinic unsaturation other than mentioned above such as poly(ethylene), poly(propylene), poly(butene-1), poly(4-methyl pentene-1), polyvinyls; e.g., poly(vinyl



chloride), poly(vinyl fluoride), poly(vinylidene chloride), poly(vinylidene fluoride), poly(vinyl alcohol), poly(vinyl esters) such as poly(vinyl acetate) and poly(vinyl propionate), poly(vinyl pyridines), poly(vinyl pyrrolidones), poly(vinyl ethers), poly(vinyl ketones), poly(vinyl aldehydes) such as  
5 poly(vinyl formal) and poly(vinyl butyral), poly(vinyl amides), poly(vinyl amines), poly(vinyl urethanes), poly(vinyl ureas), poly(vinyl phosphates), and poly(vinyl sulfates); polyallyls; poly(benzobenzimidazole); polyhydrazides; polyoxadiazoles; polytriazoles; poly(benzimidazole); polycarbodiimides; polyphosphazines; etc., and interpolymers, including block interpolymers  
10 containing repeating units from the above such as terpolymers of acrylonitrile-vinyl bromide-sodium salt of para-sulfophenylmethallyl ethers; and grafts and blends containing any of the foregoing. Typical substituents providing substituted polymers include halogens such as fluorine, chlorine and bromine; hydroxyl groups; lower alkyl groups; lower alkoxy groups;  
15 monocyclic aryl; lower acyl groups and the like.

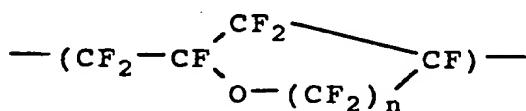
Selection of the porous separation membrane for the membrane for gas separations may be made on the basis of the heat resistance, solvent resistance, and mechanical strength of the porous separation membrane, as well as other factors dictated by the operating conditions for selective  
20 permeation, as long as the coating and porous separation membrane have the prerequisite relative separation factors in accordance with the invention for at least one pair of gases. The porous separation membrane is preferably at least partially self-supporting, and in some instances may be essentially self-supporting. The porous separation membrane may provide  
25 essentially all of the structural support for the membrane. It is emphasized that the inventive apparatus is not restricted to these particular membranes.

Particularly useful membranes are formed from a polymer having an aliphatic ring structure containing fluorine, for example, a perfluoro-2,2-dimethyl-1,3-dioxole, preferably an amorphous polymer of  
30 perfluoro-2,2-dimethyl-1,3-dioxole. In embodiments, the polymer is a homopolymer of perfluoro-2,2-dimethyl-1,3-dioxole. In other embodiments, the polymer is a copolymer of perfluoro-2,2-dimethyl-1,3-dioxole, including copolymers having a complementary amount of at least one monomer selected from the group consisting of tetrafluoroethylene, perfluoromethyl  
35 vinyl ether, vinylidene fluoride and chlorotrifluoroethylene. In preferred embodiments, the polymer is a dipolymer of perfluoro-2,2-dimethyl-1,3-dioxole and a complementary amount of

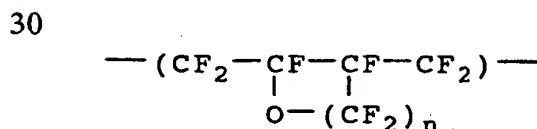


tetrafluoroethylene, especially such a polymer containing 65-99 mole % of perfluoro-2,2-dimethyl-1,3-dioxole. The amorphous polymer preferably has a glass transition temperature of at least 140°C, and more preferably at least 180°C. Glass transition temperature ( $T_g$ ) is known in the art and is the temperature at which the polymer changes from a brittle, vitreous or glassy state to a rubbery or plastic state. Examples of dipolymers are described in further detail in U.S. Patent Nos. 4,754,009 and 4,935,477 both of E. N. Squire. The polymer may also be an amorphous copolymer of perfluoro(2,2-dimethyl-1,3-dioxole) with a complementary amount of at least one other comonomer, said copolymer being selected from dipolymers with perfluoro(butenyl vinyl ether) and terpolymers with perfluoro(butenyl vinyl ether) and with a third comonomer, wherein the third comonomer can be (a) a perhaloolefin in which halogen is fluorine or chlorine, or (b) a perfluoro(alkyl vinyl ether); the amount of the third comonomer, when present, preferably being at most 40 mole % of the total composition.  $T_g$  of such dipolymers range from about 260°C for dipolymers with tetrafluoroethylene having low amounts of tetrafluoroethylene comonomer down to less than 100°C for the dipolymers containing at least 60 mole % of tetrafluoroethylene.

Other suitable polymers having an aliphatic ring structure containing fluorine are described in U.S. Patent No. 4,897,457 of Nakamura et al. and Japanese Published Patent Application Kokai 4-198918 of Nakayamura et al.; e.g., a fluorine-containing thermoplastic resinous polymer containing a group of repeating units to be represented by the following general formula:



and/or



(where:  $n$  is an integer of 1 or 2); and copolymers thereof.



Such perfluorodioxole membranes are particularly suited to the inventive membrane closure assembly because the polymer may be readily processed into a thin membrane. The membrane preferably is thin, in order to maximize the rate of gas transmission through the membrane, preferably  
5 less than 0.01 mm and especially less than 0.001 mm in thickness; in the case of composite membranes, such thickness refers to the thickness of the layer or coating of the polymer. Perfluorodioxole membranes exhibit extremely high gas transmission compared to other membranes, while also exhibiting very good selectivity. In addition, perfluorodioxole membranes exhibit  
10 essentially constant performance over a wide range of temperatures.

Perfluorodioxole materials have relatively high permeability constants for fluids such that it does not unduly reduce the permeation rate of the membrane for desired components. Moreover, organic compounds such as toluene do not adversely interact with the membrane so as to impair  
15 permeation rates. In addition, perfluorodioxole membranes are long lasting and inert to most organic compounds. It is also believed that perfluorodioxole membranes are resistant to the effects of impurities such as dirt or water vapor.

Perfluorodioxole membranes may be manufactured by a variety  
20 of methods known to those skilled in the art, particularly in the light of the versatile processability of the perfluorodioxole polymers. These methods include solvent and melt film-casting and fibre-casting methods, as well as coating techniques; other fluoropolymers tend to be either melt processible but not solvent processible or not processible by either method.

25 The gaseous admixture fed to the membrane separation cell may be an admixture of nitrogen, usually containing oxygen and especially in the form of air, and a gaseous organic compound(s). The gaseous organic compound may be a compound that is a gas at atmospheric temperature and pressure, but will more commonly be the vapor of an organic compound that  
30 is in liquid form at atmospheric pressure and temperature. The gaseous admixture will usually be at about ambient temperature but may be at higher temperatures; the membranes used in the method of the present invention are capable of being used at elevated temperature, including in some embodiments at temperatures about 100°C. However, perfluorodioxole  
35 membranes preferably should be used at a temperature below the glass transition temperature, and especially at least 30°C below the glass transition temperature, of the amorphous polymer used to form the membrane. In



preferred embodiments, the glass transition temperature of the perfluorodioxole membrane is at least 140°C, preferably at least 180°C and most preferably about 240°C. The method of the present invention may be operated at relatively low temperatures; e.g., as low as about -50°C, and especially about 15°C.

5 The gaseous admixture may be vapors from a fuel tank or storage vessel for gasoline, heating oil, jet fuel or the like. The admixture may be from a process for the manufacture of foamed materials, in which event the organic compound may be a fluorocarbon or hydrocarbon of the type used in such processes. Alternatively, the admixture may be from a dry-cleaning process in which event the organic compound may be a hydrocarbon or chlorinated hydrocarbon, or from a coating process in which event the organic compound may be mixtures of aromatic and aliphatic hydrocarbons and derivatives thereof; e.g., ethers, alcohols and the like. The gaseous admixtures may contain a wide range of amounts of organic compounds. The permeate should normally not contain an amount of organic compounds that preferably should not or cannot be discharged to the atmosphere because of regulatory or other reasons.

It will be appreciated that a wide range of organic compounds may advantageously be used with the apparatus of the present invention. Examples of such compounds include butane, pentane, hexane, septane, octane, and fluorocarbons; e.g., trichloromonofluoromethane, dichlorodifluoromethane, monochlorotrifluoromethane, trichlorotrifluoroethane, dichlorotetrafluoroethane, monochloropentafluoroethane,  $\text{CF}_3\text{CH}_2\text{F}$ , toluene, xylene, naphtha and other mixed hydrocarbon fractions, chlorinated hydrocarbon solvents, polar organic compounds; e.g., methyl ethyl ketone, and the like.

As exemplified hereinafter, oxygen and nitrogen are preferentially passed through the membrane, especially at relatively low concentrations of the organic compound. Thus, the feed stream is enriched in the organic compound. Moreover, oxygen and nitrogen pass through the membrane at a high rate; i.e., there is high flux rate, which is necessary in order that use of the present membrane closure assembly be of commercial interest.

35 The pressure normalized flux of gases through membranes can be defined as:



$$1 \text{ GPU} = \frac{10^{-6} \text{ cm}^3 (\text{STP})}{\text{cm}^2 \times \text{sec.} \times \text{cm Hg}}$$

5 wherein  $\text{cm}^3 (\text{STP})/\text{sec}$  is the flux (flow rate) in units volume per seconds of permeated gas at standard temperatures and pressure,  $\text{cm}^2$  is the area of film, and cm Hg is the pressure (or driving force).

The selectivity of a membrane in separating a 50/50 mixture of a two-component fluid is defined as the ratio of the rate of passage of the more readily passed component to the rate of passage of the less readily passed component. Selectivity may be obtained directly by contacting a membrane with a known mixture of fluids and analyzing the permeate. Alternatively, a first approximation of the selectivity is obtained by calculating the ratio of the rates of passage of the two components determined separately on the same membrane under equivalent driving pressure differences. Rates of passage may be expressed GPU units. As an example of selectivity, a  $\text{O}_2/\text{N}_2 = 10$  indicates that the subject membrane allows oxygen gas to pass through a rate 10 times that of nitrogen for a 50/50 feed mixture.

20

#### EXAMPLES

The present invention is illustrated by the following examples.

##### Example I

Membranes with a thickness of 0.25 mm were melt-pressed from three dipolymers of perfluoro-2,2-dimethyl-1,3-dioxole and tetrafluoroethylene of different dioxole contents and glass transition temperatures ( $T_g$ ). Single-gas permeation tests were conducted using a membrane prepared from a membrane of this high- $T_g$  dipolymer. A number of different gases were tested. As a comparison, tests were also conducted on a membrane formed from polytetrafluoroethylene (PTFE).

30 A number of permeability measurements were conducted, using pressures that were generally in the range of 350-1750 kPa, it being the understanding that the permeability of the gases listed in Table I is only a slight function of pressure in this pressure range. An exception to this understanding may be carbon dioxide, and the pressure used for this gas was 1750 kPa.

The results obtained are given in Table I.



TABLE I

Gas	Permeability	
	Dipolymer	PTFE
CO <sub>2</sub>	2800 Barrer	12 Barrer
He	2700 Barrer	
H <sub>2</sub>	2200 Barrer	9.8 Barrer
O <sub>2</sub>	990 Barrer	4.2 Barrer
N <sub>2</sub>	490 Barrer	1.4 Barrer
Ethylene	350 Barrer	
Methane	340 Barrer	
Ethane	180 Barrer	

The results obtained illustrate the high permeability obtainable with the membranes of the present invention. Whereas the selectivity demonstrated by the dipolymer and polytetrafluoroethylene membranes are similar, and believed to be relatively typical of glassy, nonrubbery polymers, the dipolymer membranes exhibit relatively very high permeability.

#### Example II

Permeation measurements were conducted using a permeation cell that was immersed in water in a temperature-controlled water bath. The permeate from the permeation cell was passed through a sampler bulb of a gas chromatograph, to measure the composition of the permeate, and then to a soap film capillary to measure the permeate flow rate. Concentrations in gas mixtures were measured with a HP Gas Chromatograph Model 5700A followed by a Spectra Physics Integrator type Model SP4400. Pressure and pressure drop could be measured in the cell.

The membrane was placed on a porous sinter (pore size 15-20 microns) and held in place using two TEFLON® rings. The effective membrane area for mass transfer was 9.62 cm<sup>2</sup> (3.5 cm diameter).

When mixtures of gases were being tested, a purging stream with about 10 times the permeate flow rate was used to ensure a constant feed concentration, and the purged stream was monitored to determine the feed concentration. For measurements with single gases, the cell was purged at the beginning of each experiment for a short period of time.

Melt pressed membranes were prepared by placing polymer in a mold and heating to a temperature of about 20°C above the glass transition



temperature ( $T_g$ ). When that temperature was reached, the polymer was treated by applying pressure and releasing it, using pressures of up to 50 tonnes/12.5 cm diameter of the membrane, for 5 minutes. The mold was then slowly cooled under a pressure of 40 tonnes/12.5 cm diameter, to room temperature. The resultant thick powder was transferred to the center of a flat plate covered by aluminum foil. Another aluminum foil-covered flat plate was mounted on it, without any spacer. The two plates were heated in a melt press, at minimal pressure, to a temperature of 100°C above  $T_g$ , after which the pressure was raised to 40 tonne/12.5 cm diameter, and the sample was pressed for 10 minutes. The sample was then cooled slowly to room temperature under pressure, and the aluminum foil was peeled off carefully.

Cast membranes were prepared from solutions of the polymers in FC-75 solvent. The solution was warmed to 50-60°C, and filtered through a 3 micron filter. The filtered solution was cast onto clean glass, and dried at ambient temperature in a dust-free environment. The membrane was further dried in an oven at 80°C for at least 2 hours, and then in an oven at 110°C overnight.

Membranes were formed from a dipolymer of perfluoro-2,2-dimethyl-1,3-dioxole and tetrafluoroethylene having a glass transition temperature of 240°C, by solvent casting from a 2.5% solution in FC-75 solvent using the procedure described above, with the heating at 110°C being for 12 hours. The resultant membrane was 20 micron thick.

The mixed gas fed to the permeation cell had the following composition: N<sub>2</sub>, 78.25%; O<sub>2</sub>, 260.67%; and CFC-12, 1.0%.

Further experimental details and the results obtained are given in Table II. Measurements were made at 20°C under steady-state conditions in this and the following examples, unless stated to the contrary.

TABLE II

Pressure (kPa)	Permeability (Barrers)			Selectivity	
	O <sub>2</sub>	N <sub>2</sub>	CFC-12	O <sub>2</sub> /N <sub>2</sub>	N <sub>2</sub> /CFC-12
700	242	114	16	2.1	7.1
445	263	112	11	2.4	10.3

The results show that the selectivity to the fluorocarbon gas is dependent on the pressure used in the process, improving at lower pressures.



Example III

Membranes were prepared from a number of different polymers of perfluoro-2,2-dimethyl 1,3-dioxole, using the solvent casting method described in Example II. The membranes were tested for permeability using the gaseous mixture of Example II.

Further details and the results obtained are given in Table III.

TABLE III

Polymer*	Pressure (kPa)	Permeability (Barrers)			Selectivity	
		O <sub>2</sub>	N <sub>2</sub>	CFC-12	O <sub>2</sub> /N <sub>2</sub>	N <sub>2</sub> /CFC-12
A	790	444	332	203	1.3	1.6
	445	463	306	63	1.5	4.8
B	790	586	444	362	1.3	1.2
	445	505	436	317	1.3	1.4
C	790	2097	1143	312	1.8	3.7
	445	2228	1165	211	1.8	5.5
	240	2200	1166	160	1.9	7.3

\*A = Copolymer of perfluoro methyl vinyl ether and perfluoro-2,2-dimethyl-1,3-dioxole, with a  $T_g$  of 139°C; membrane thickness was 15 microns.

B = Copolymer of chlorotrifluoroethylene and perfluoro-2,2-dimethyl-1,3-dioxole, with a  $T_g$  of 157°C; membrane thickness was 13 microns.

C = Homopolymer of perfluoro-2,2-dimethyl 1,3-dioxole, with a  $T_g$  of 330°C; membrane thickness was 17 microns.

The results show that the homopolymer exhibits high permeation rates. The homopolymer and copolymer with perfluoromethyl vinyl ether exhibit significant selectivity of nitrogen over the fluorocarbon gas.

Example IV

A copolymer of perfluoro(methyl vinyl ether) and perfluoro-2,2-dimethyl-1,3-dioxole having a  $T_g$  of 139°C was solvent cast into membranes from a 10% solution of the polymer in FC-75 solvent and dried as described in Example II. A second membrane was prepared in the same manner, except that the membrane was heated to a temperature above the



$T_g$ , to a temperature of 150°C for an additional hour. Both membranes were tested with single gases.

The results obtained are given in Table IV below:

TABLE IV

Membrane Thickness (microns)	Temperature of Drying	Permeability $N_2$ /CFC-12	Selectivity Barrers $N_2$ /CFC-12
55	Below $T_g$	47/12	3.9
63	Above $T_g$	63/18	3.8

5 The results show that, for the polymer from which the membrane was formed, heating the membrane above the glass transition point gave an apparent modest increase in the permeability of the membrane but did not affect the selectivity of the membrane under the conditions used.

#### 10 Example V

Membranes formed from poly-[perfluoro(2-methylene-4-methyl-1,3-dioxolane)]; i.e., polymer of the aforementioned U.S. Patent No. 3,308,107, had been tested for permeability using a volumetric method at 25°C.

15 Further experimental details and the results outlined are given in Table V.

TABLE V

Gas	Permeability	Gas	Permeability
He	650 Barrers	$H_2$	240 Barrers
$CO_2^*$	67 Barrers	CO	8 Barrers
$CH_4^*$	2 Barrers	$O_2^*$	36 Barrers
$N_2^*$	10 Barrers		

\*Results are averages of data for single gases and binary mixtures.

20 It is believed that the permeability data for methane may be in error, being smaller than would be expected.

#### Example VI

25 Permeability measurements were conducted on a variety of membranes, formed by melt pressing or by solvent casting. The method of measurement of permeability was that described in Example II. The gases



used were nitrogen and CFC-12, the permeabilities for which were measured separately.

Further experimental details and the results obtained are given in Table VI.

5

TABLE VI

Polymers	Permeability (Barrers)		Selectivity (N <sub>2</sub> /CFC-12)
	N <sub>2</sub>	CFC-12	
E	555	26	21
F	2725	1168	2.3
G	63	18	3.5
H	53	2.5	21
J	49	53	0.92

\*E = Copolymer of perfluoro-2,2-dimethyl-1,3-dioxole and tetrafluoroethylene,  $T_g = 240^\circ\text{C}$ , thickness = 80 microns, formed by melt pressing, pressure used was 6 psig;

10 F = Homopolymer of perfluoro-2,2-dimethyl 1,3-dioxole, with a  $T_g = 330^\circ\text{C}$ ; thickness = 24 microns, formed by solvent casting from FC-75 solvent, pressure used was 5 psig;

G = Copolymer of perfluoro-2,2-dimethyl-1,3-dioxole and perfluoromethyl vinyl ether,  $T_g = 137^\circ\text{C}$ , thickness = 63 microns, formed by solvent casting from FC-75 solvent, pressure used was 5 psig;

15 H = Copolymer of vinylidene fluoride and perfluoro-2,2-dimethyl-1,3-dioxole, with a  $T_g$  of  $82^\circ\text{C}$ ; thickness = 55 microns, formed by solvent casting from FC-75 solvent, pressure used was 25 psig. Note: at a lower pressure, no flux of CFC-12 was observed;

20 J = Copolymer of perfluoro-2,2-dimethyl-1,3-dioxole and tetrafluoroethylene,  $T_g = 160^\circ\text{C}$ , thickness = 200 microns, formed by melt pressing, pressure used was 5 psig.

The results show effects of comonomer on permeability and selectivity to nitrogen and CFC-12.

25

#### Example VII

Using procedures described above, membranes were melt pressed from a copolymer of perfluoro-2,2-dimethyl-1,3-dioxole and tetrafluoroethylene having a  $T_g = 240^\circ\text{C}$ . Permeation tests were conducted



using mixtures of oxygen, nitrogen and a fluorocarbon gas or of nitrogen and a hydrocarbon gas.

Further experimental details and the results obtained are given in Table VII.

5

TABLE VII

Gas Mixture	Permeability (Barrers)			Selectivity		Flux (ml/sec)
	N <sub>2</sub>	O <sub>2</sub>	CFC	N <sub>2</sub> /CFC	O <sub>2</sub> /N <sub>2</sub>	
(a) Membrane thickness 200 microns						
A	505	1005	41	12.5	2.0	0.0152
B	255	480	4	61	1.9	0.0082
C	535	1065	<3	>100	2.0	0.0156
D	555	1080	37	15	1.9	0.0161
E	570	1130	71	8	2.0	0.0167
F	405	-	55	7.4	-	0.0100
(b) Membrane thickness 80 microns						
A	300	590	40	7.5	2.0	0.0217
B	215	450	15	14	2.1	0.0161
C	290	565	9	31	1.9	0.0208
D	350	640	28	12.5	1.8	0.0250
E	365	700	49	7.5	1.9	0.0263
F	385	-	130	3	-	0.0238

Note: The membranes shown in the Table were prepared from the same polymer but in different laboratories.

Gas mixture A = CFC 12 (MW = 120.9):air in ratio of 1:99

Gas mixture B = HCFC 123 (MW = 152.9):air in ratio of 0.43:99.57

10 Gas mixture C = CFC 114 (MW = 170.9):air in a ratio of 1:99

Gas mixture D = HCFC 142b (MW = 100.5):air in a ratio of 1:99

Gas mixture E = HCFC 134a (MW = 102.0):air in ratio of 1:99

Gas mixture F = butane (MW = 58.1):nitrogen in a ratio of 1:99

15

The results show a correlation of increasing selectivity with increasing molecular weight of the fluorocarbon gas or hydrocarbon gas. In one of the membranes, the two highest molecular weight gases had selectivities of above 100 and 60, respectively. On the basis of the above



results, it would appear that selectivity is related to molecular size, rather than whether the gas is a fluorocarbon or a hydrocarbon.

### Example VIII

5           The membranes of Example VII were tested using single gases viz. nitrogen, toluene vapor, water vapor and butane gas, and in one instance using nitrogen saturated with toluene; the latter was achieved by passing nitrogen over the surface of liquid toluene and feeding the resultant stream to the membrane. In addition, a membrane made by solvent casting the  
10   homopolymer of perfluoro-2,2-dimethyl-1,3-dioxole was tested using butane and nitrogen. Although the nitrogen permeabilities were measured at 790 kPa, it is known from results given above that the permeability for that gas is independent of pressure; comparison may therefore be made with the results obtained with the other gases and vapors.

15           The results are given in Table VIII.

TABLE VIII

Vapor/Gas	Membrane	Temp. (°C)	Pressure Differential (kPa)	Permeability (Barrer)
Toluene	A	25	4.1	0
Toluene	A	52	13	0
Butane	A	25	110	0
Butane	B	25	90	0
Butane	C*	25	100	9000
Nitrogen	A	25	790	580
Nitrogen	B	25	790	620
Nitrogen	C	25	790	1675
Water	A	70	32	3000**
Water	A	25	3.4	100
Nitrogen (saturated with toluene)	A	25	340	575

Note: \*O<sub>2</sub>/N<sub>2</sub> selectivity was measured on the membrane used in this test, and was found to be 1.9. This is confirmation of the integrity of the membrane.



\*\*At 25°C and a pressure drop of 3.2 kPa, the permeability to water was considerably lower.

Membrane A was the melt cast membrane of Example VII, thickness = 200 microns.

5 Membrane B was the melt cast membrane of Example VII, thickness = 80 microns.

Membrane C was formed from the homopolymer by solvent casting, thickness = 100 microns.

10 The results show that very high selectivities were obtained for the melt pressed membranes, whereas the homopolymer membrane appears to be selective to butane in single gas measurements; results report above would indicate that significantly lower selectivity could be expected with mixed gases.

15

#### Example IX

A membrane of the homopolymer of perfluoro-2,2-dimethyl-1,3-dioxole was prepared using the solvent casting technique described in Example II; the membrane thickness 33 microns. It  
20 was tested for permeability using synthetic air and several single gases with a feed pressure of 790 kPa.

The results obtained are given in Table IX.

TABLE IX

Gas	Permeability (24°C)
He	3600 Barrer
H <sub>2</sub>	3300 Barrer
O <sub>2</sub> (air feed)	1540 Barrer
N <sub>2</sub> (air feed)	810 Barrer
N <sub>2</sub>	830 Barrer
CH <sub>4</sub>	690 Barrer
C <sub>2</sub> H <sub>6</sub>	500 Barrer

25 It is believed that the permeabilities of hydrogen and helium are the highest measured with these gases, with the exception of polytrimethylsilylpropyne. The latter polymer, however, is known to have unstable gas transport properties; e.g., see U.S. 4,859,215.



Moreover, the permeability of nitrogen in mixed gas tests was similar to the permeability of nitrogen in single gas tests, which indicates that there was no measurable interaction between copermeating oxygen and nitrogen molecules or competition for permeation paths in the polymer.



**WHAT IS CLAIMED IS:**

1. A membrane closure apparatus comprising:
  - a. a plurality of hollow fiber membrane with bores therethrough and walls which are selectively permeable to one or more gases in an admixture of gases, said membranes being assembled into a bundle;
  - b. at least one end of the bundle being embedded in a tubesheet;
  - c. an inlet port or opening in fluid communication with an admixture of gases contained in a tank, said admixture having at least one organic gas;
  - d. a residue discharge port in fluid communication with the bores of the membranes;
  - e. said hollow fiber membranes having a selective permeation of nitrogen over said organic gas of at least 10:1.
2. The apparatus of claim 1 in which the membrane is formed from an amorphous polymer of perfluoro-2,2-dimethyl-1,3-dioxole.
3. The apparatus of claim 1 in which the membrane is a supported membrane.
4. The apparatus of claim 1 in which the membrane is in the form of a hollow fiber.
5. The apparatus of claim 1 in which the membrane is in the form of a film or coating on a porous support.
6. The apparatus of claim 2 in which the polymer is a copolymer of perfluoro-2,2-dimethyl-1,3-dioxole.
7. The apparatus of claim 6 in which the polymer is a copolymer of perfluoro-2,2-dimethyl-1,3-dioxole and a complementary amount of at least one monomer selected from the group consisting of tetrafluoroethylene, perfluoromethyl vinyl ether, vinylidene fluoride and chlorotrifluoroethylene.
8. The apparatus of claim 2 in which the polymer is a homopolymer of perfluoro-2,2-dimethyl-1,3-dioxole.
9. The apparatus of claim 7 in which the polymer is a dipolymer of perfluoro-2,2-dimethyl-1,3-dioxole and a complementary amount of tetrafluoroethylene.



10. The apparatus of claim 9 in which the polymer is a dipolymer containing 65-99 mole % of perfluoro-2,2-dimethyl-1,3-dioxole and having a glass transition temperature of at least 140°C.

5 11. The apparatus of claim 1 further comprising a permeate discharge port which is in fluid communication with the outside surface of the membranes.

12. The apparatus of claim 1 wherein the hollow fiber membranes are substantially perpendicular to the flow of the gas admixture.

10 13. The apparatus of claim 1 which is further engaged with the filler tube of a fuel tank or the vent line of a storage tank for preventing the outflow of organic vapors.

14. The apparatus of claim 1 further comprising a bundle of hollow fiber membranes having a central axial opening therein.

15 15. A method for preventing the outflow of organic vapors from a container comprising: providing in a membrane separation cell a selectively permeable membrane having a feed side and a permeate side, and the feed side of said membrane separation cell being in communication with the organic vapor.

20 16. The method of claim 15 in which the pressure differential is applied across the membrane.

17. The method of claim 15 in which the membrane has a selective permeation of nitrogen over the organic compound of at least 10:1.

18. The method of claim 15 in which the organic vapor is gasoline, heating oil or jet fuel.

25 19. The method claim 15 in which the membrane is formed from an amorphous polymer of perfluoro-2,2-dimethyl-1,3-dioxole.

30 20. The method of claim 19 in which the polymer is a copolymer of perfluoro-2,2-dimethyl-1,3-dioxole and a complementary amount of at least one monomer selected from the group consisting of tetrafluoroethylene, perfluoromethyl vinyl ether, vinylidene fluoride and chlorotrifluoroethylene.

21. The method of claim 19 in which the polymer is a homopolymer of perfluoro-2,2-dimethyl-1,3-dioxole.

35 22. The method of claim 19 in which the polymer is a dipolymer of perfluoro-2,2-dimethyl-1,3-dioxole and a complementary amount of tetrafluoroethylene.



23. The method of claim 19 in which the polymer is a dipolymer containing 65-99 mole % of perfluoro-2,2-dimethyl-1,3-dioxole and having a glass transition temperature of at least 140°C.



FIG. 1

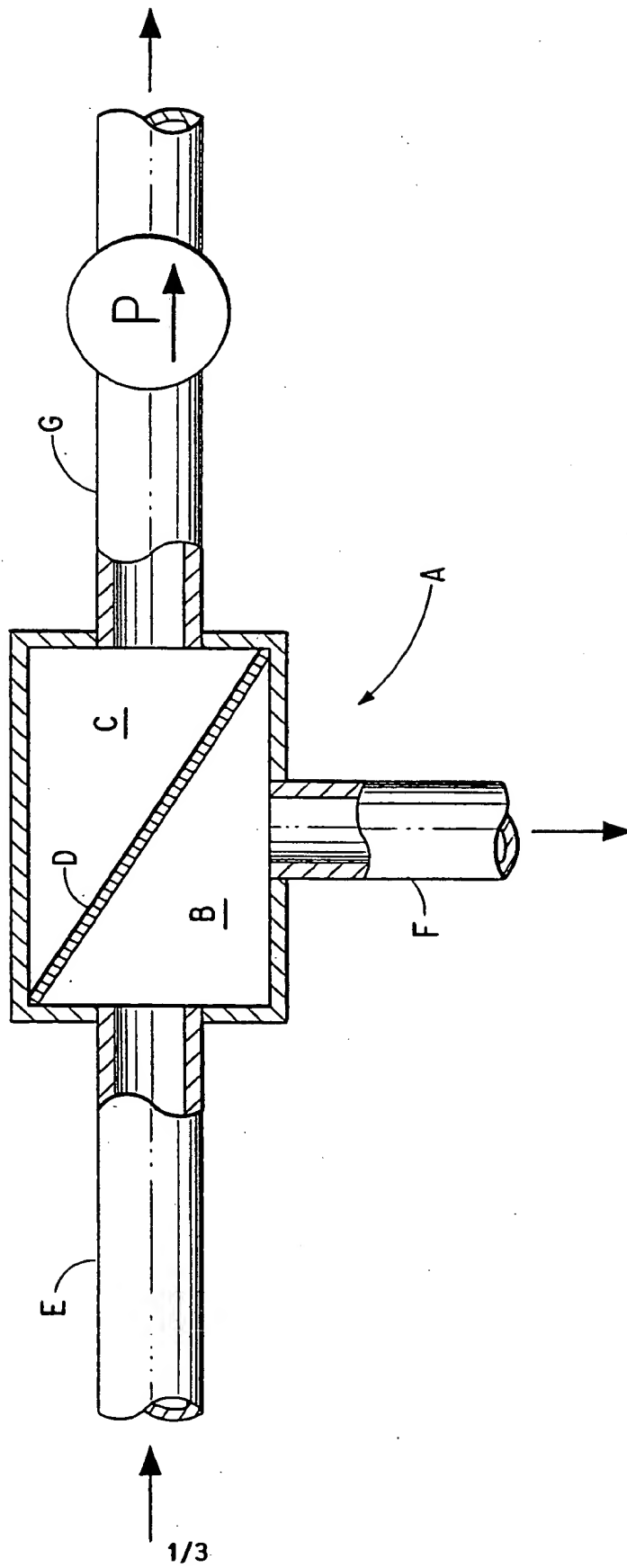




FIG. 3

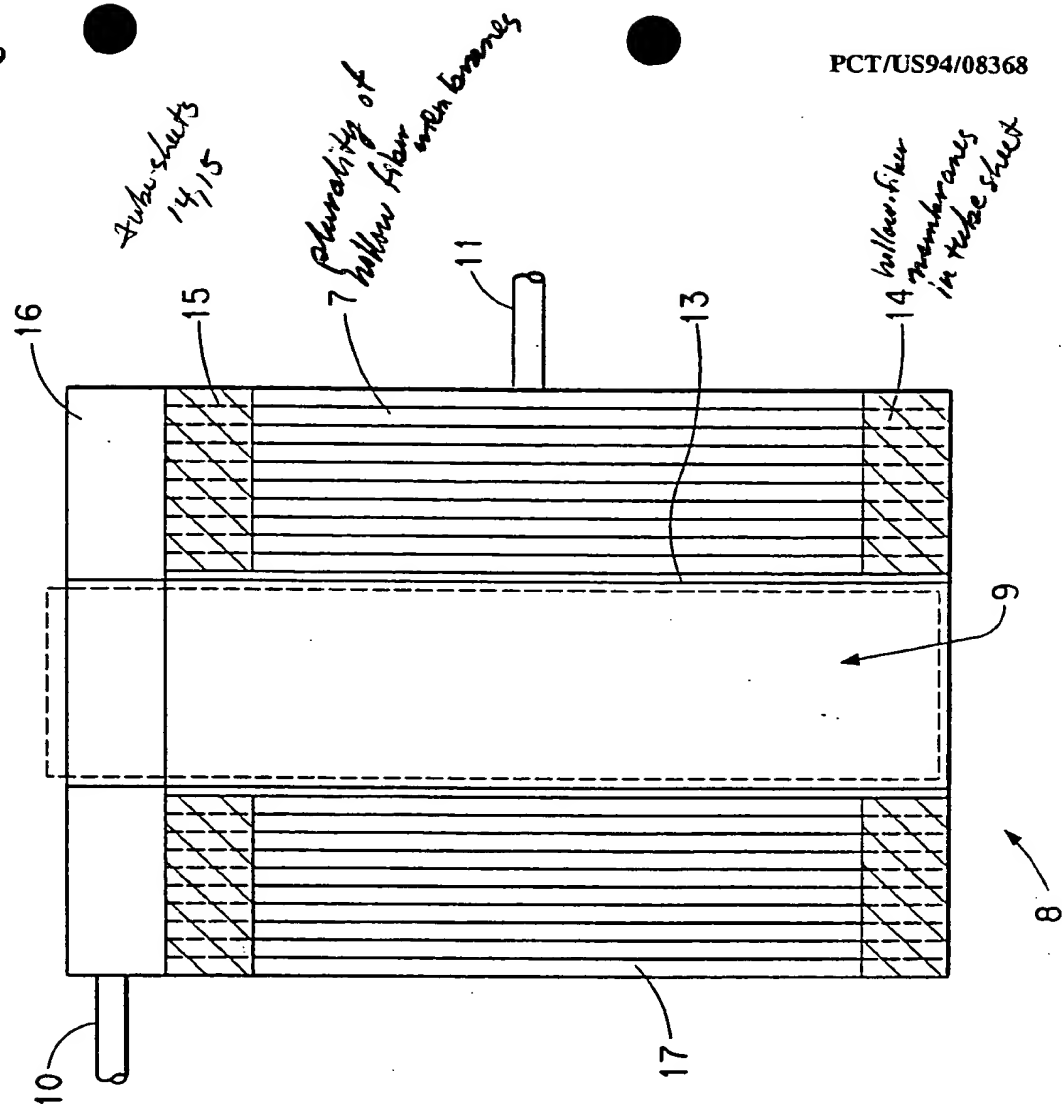


FIG. 2

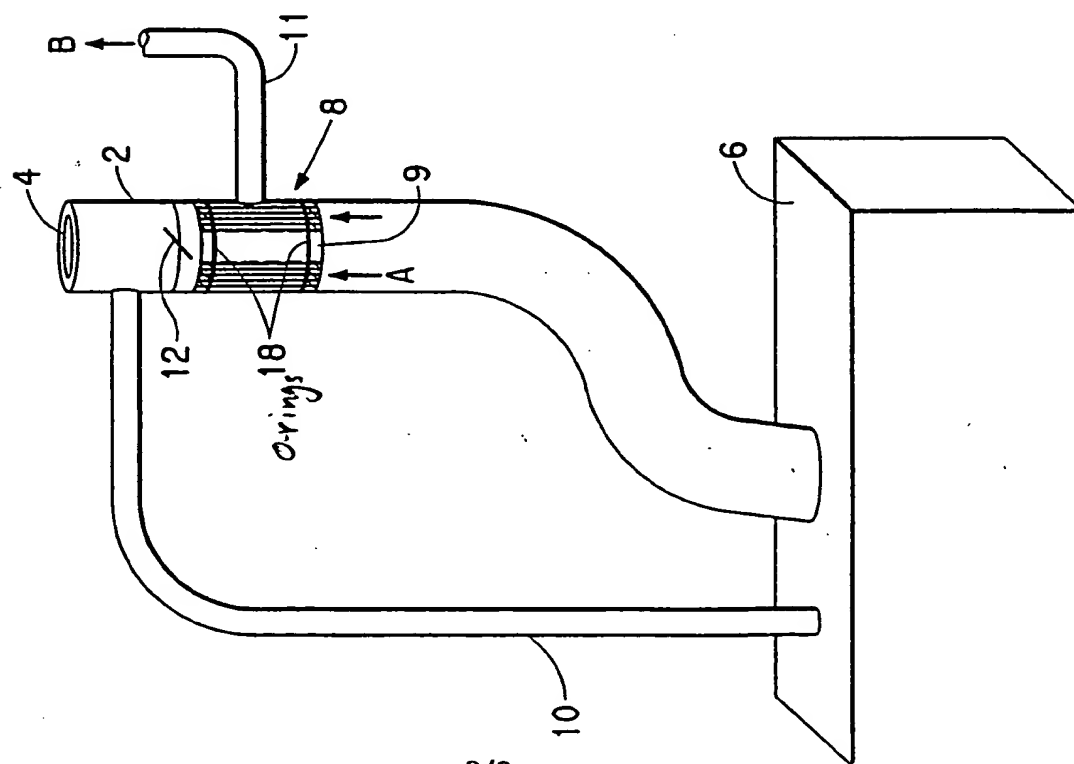
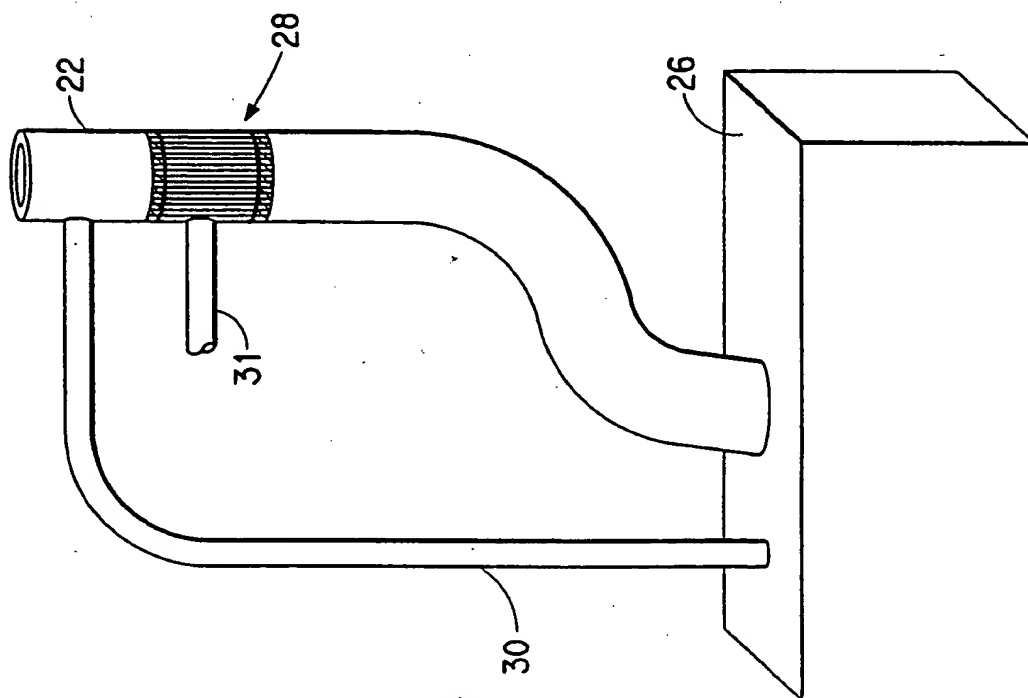


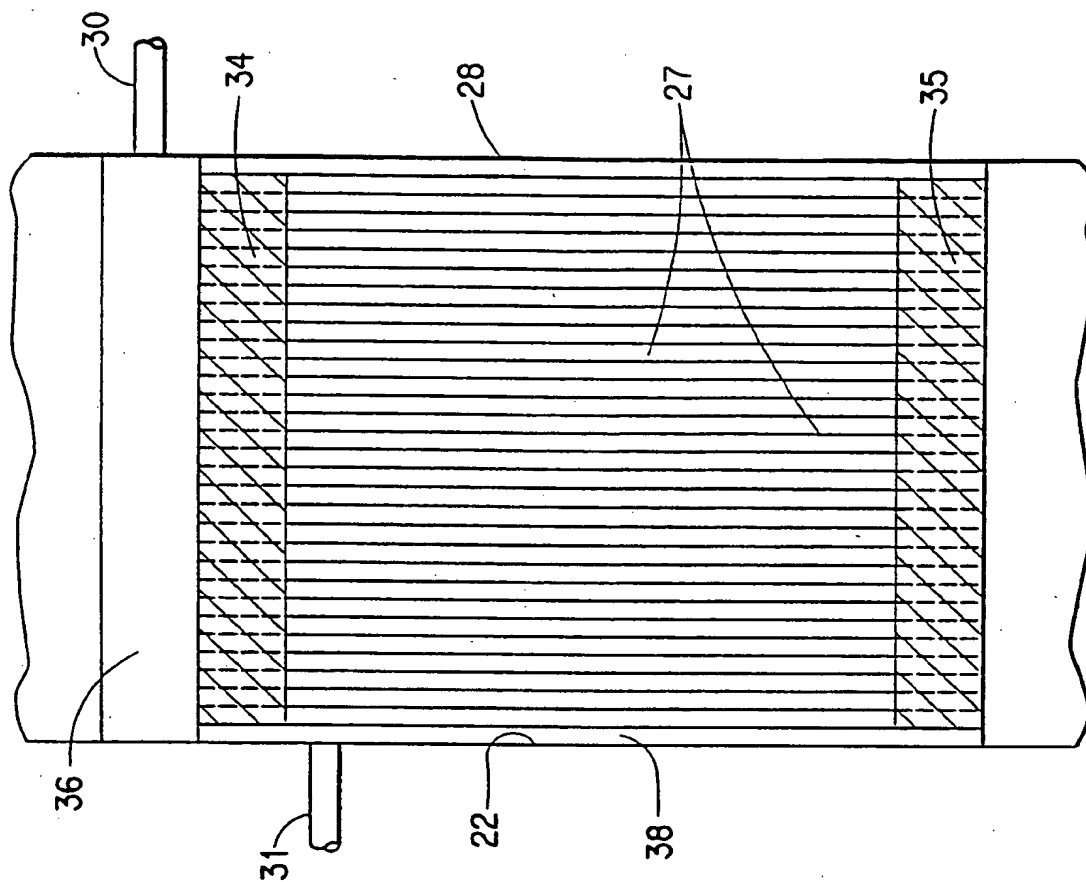


FIG. 4



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FIG. 5





## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 94/08368

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B60K15/035 B60K15/04 B65D51/16 B01D53/22 B01D63/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B60K B65D B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,90 15662 (DU PONT CANADA INC) 27 December 1990 see abstract; claims 1,6-17,23-27; figure 1 see page 1, line 5 - line 15 see page 3, line 4 - page 4, line 16 see page 5, line 24 - page 7, line 19 see page 8, line 3 - line 8 see page 9, line 15 - page 11, line 5 see page 11, line 19 - line 27	15-23
Y	---	1-14
X	DE,A,40 06 465 (FRAUNHOFER GES) 5 September 1991 see the whole document	15, 16, 18
Y	---	1-14
	--- -/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

17 November 1994

Date of mailing of the international search report

21. 12. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Hoornaert, P



# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 94/08368

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 461 852 (DU PONT CANADA INC) 18 December 1991 see abstract; claims 1,7,8; figures 1,2 see page 2, line 45 - page 3, line 58 ---	1-12
X	DE,U,92 05 925 (GKSS) 3 December 1992 see claims; figure see page 11 ---	15,16,18
X	PATENT ABSTRACTS OF JAPAN vol. 15, no. 202 (C-0834) 23 May 1991 & JP,A,03 056 114 (NITTO DENKO CORP) 11 March 1991 see abstract & DATABASE WPI Section Ch, Week 9116, Derwent Publications Ltd., London, GB; Class J01, AN 91-114325 see abstract ---	15,16
A	US,A,5 042 678 (MUNGULA) 27 August 1991 cited in the application see the whole document -----	1,13,14



## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.  
PCT/US 94/08368

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DE-U-9205925	03-12-92	NONE	
US-A-5042678	27-08-91	NONE	



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